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Laboratory Experiment

An Environmental Forensic Chemistry Experiment Involving Abandoned Mine Drainage Remediation

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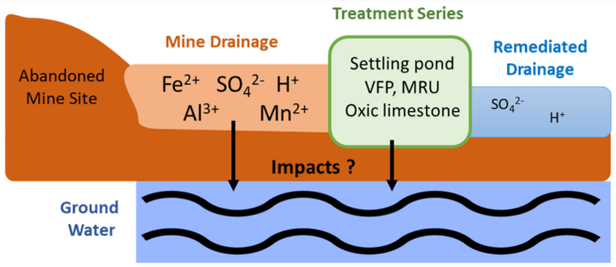

ABSTRACT: Most forensic chemistry experiments focus on the usual suspects involving criminal scenarios: illicit drug identification, gunshot residue detection, blood and fingerprint analysis, and arson investigations. However, environmental forensics involves chemical techniques that can expand the breadth of experience for forensic chemistry students. An experimental case study was designed to determine the potential source of groundwater contamination along a series of treatment steps designed to mitigate the environmental effects of an abandoned mine drainage site. Simulated drainage samples representing each treatment step are analyzed by atomic absorption spectroscopy to quantify the metals present, a gravimetric method to determine the concentration of sulfate, and a pH meter to measure relative acidity of the drainage water. Using the data obtained from the simulated samples, students can determine the effectiveness of each treatment step as well as identify the location along the drainage treatment series that is the most likely source of the groundwater contamination.

KEYWORDS: *Analytical Chemistry, Environmental Chemistry, Acids/Bases, Metals, pH, Spectroscopy, Gravimetric Analysis, Forensic Chemistry*

■ INTRODUCTION

Forensic science involves the use of science and technology to investigate various aspects of potential or confirmed criminal or civil violations and encompasses many different fields (digital, psychological, ballistic, accounting, environmental, etc.). The most popular fields for study at the undergraduate level involve the examination of biological (hair, blood, and DNA) and chemical (drugs, fingerprints, materials, and residues) trace evidence. Most experiments prepared for undergraduate forensic chemistry laboratories involve techniques to analyze trace evidence: qualitative wet chemical testing, paper or thin layer chromatography, staining for microscopy, and separation/identification of analytes using laboratory instruments (UV−vis, FTIR, HPLC, GC, and GC−MS). Many experiments and case studies using these methods have been published in this *Journal*[1−7] and elsewhere.[8−11] However, the practice of additional chemical techniques educates the students about the broader spectrum of analytical work performed by forensic chemists.

Environmental forensic chemistry investigations, which examine the extent, duration, and sources of environmental contamination, are picking up steam as European and U.S. policies are leading to increased enforcement and litigation cases.[12,13] At Harrisburg University of Science and Technology, a bachelor of science degree in integrative sciences defines environmental science and forensics as two of the five concentration options available for completion of the program. Therefore, an environmental chemistry forensic case study was developed to engage students involved with different program disciplines and introduce them to another expanding field of forensics.

The new case study focused on producing experimental results to trace the source of groundwater contamination from a series of treatment steps installed to diminish environmental effects of an abandoned mine drainage (AMD) site. AMD has contaminated over 5500 miles of streams and groundwaters in Pennsylvania and remains the top environmental threat to the four main water basins in the state.[14,15] The metals, solids, and acidity of drainage from abandoned mine sites can pollute groundwater sources and also disrupt the ecology of surface waters. Different treatment strategies exist to remediate AMD based on the chemical properties of the drainage present at each site.[16−18] In the environmental case study presented here, contamination of groundwater near an acid mine drainage remediation tract has been detected by elevated levels of sulfate and manganese in a nearby residential drinking well. Students analyzed samples for metals, sulfate, and pH from various treatment steps in the tract while also using appropriate

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documentation for traceability and quality control measures for reliability of results. Using critical thinking skills, students assessed which steps in the tract were the most effective in decreasing AMD components and described the chemistry occurring along the tract. By comparing the experimental results to those found in the drinking water well, the potential areas where the drainage flow may be escaping into the groundwater were correctly identified.

CASE STUDY OVERVIEW

The variety of geologic characteristics of abandoned mines results in unique types of drainage chemistry that must be assessed to design effective treatment strategies. The utility of various mine drainage treatments based on chemical assessment was presented during a lecture session in an upper level undergraduate forensic chemistry course populated by six integrative science majors with concentrations in forensics and chemistry. Students had been instructed in and employed proper use of sample and procedural documentation and quality controls in previous experiments. Student preparation for the experimental portion of this case study required viewing YouTube videos demonstrating how atomic absorption spectroscopy works[19−21] and preparing laboratory notebooks using the supplied Standard Operating Procedure (SOP) for analysis of mine drainage samples (see Supporting Information).

The case study presented to students explains that a residential well located near an AMD remediation tract has shown increased levels of sulfate and manganese concentrations (see Table 1). This indicates that the groundwater underneath the drainage treatment steps is potentially being impacted by the mine drainage flow. Students received a set of samples along with a sample submission sheet indicating the collection location of the mine drainage flow at the mine exit site or after one of the treatment steps. One neat sample was submitted for analysis of pH and sulfate, and one sample preserved with nitric acid (to a pH < 2) was required for metal analysis. Students analyzed the samples according to the SOP, entered results into a collective spreadsheet, and used the class data to evaluate the utility of each treatment step and determine the location(s) in the tract where drainage flow may be impacting the groundwater.

Table 1. Evidence from Well near AMD Tract

pH	7.10
Sulfateion (ppm)	395
Fe (ppm)	<1.00
Mn (ppm)	9.55
Al (ppm)	<1.00

EQUIPMENT AND SUPPLIES

Instructions for the preparation of samples containing representative pH levels and concentrations of iron, manganese, aluminum, and sulfate are provided in the Supporting Information. The pH measurement can be performed with field pH electrodes or any benchtop meter calibrated using standard buffers of pH 4, 7, and 10. The gravimetric analysis of sulfate requires standard laboratory glassware, volumetric glass pipets, a heated magnetic stir plate, barium chloride, hydrochloric acid, a vacuum filtration apparatus, and an analytical balance. The concentration of iron and manganese in each sample was determined using a Shimazu AA-7000 series atomic absorption spectrometer with an air−acetylene gas oxidant/fuel combination along with metal specific cathode tubes. Note that analysis of aluminum requires a nitrous oxide−acetylene gas oxidant/fuel combination. Nitric acid was employed for sample pH adjustments, and the instrument calibration curve solutions were prepared from a 100 ppm mixed metal standard solution.

PROCEDURE SUMMARY

The forensic chemistry course met for two 75 min lecture sessions and one 3 h laboratory session per week. In the laboratory session, students measured pH, began precipitation of sulfate, and prepared samples/calibration standards for atomic absorption analysis to run via an autosampler. In the subsequent lecture session, students filtered the settled sulfate solids, received the spectroscopy results, and recorded all data in the collective spreadsheet. The case study can be completed in one laboratory session if standard curve solutions are previously prepared and the sulfate precipitant is filtered after settling for 1 h (this may decrease the recovery level of the sulfate ion). Two laboratory sessions would be needed if manual sample injection is required for atomic absorption spectroscopy.

Students began analysis for sulfate by adding 10 drops of concentrated hydrochloric acid to each 100 mL aliquot of the neat drainage sample and a 100 mL aliquot of distilled water. The aliquots were heated and stirred during slow addition of aliquots (about 1 mL per minute) of a 20 mL solution of 0.10 M $BaCl_2$. As the heated precipitation samples stirred for 1 h, students determined the pH of a 50 mL aliquot from the neat drainage sample using an Oakton pH 510 series meter and prepared four standard calibration solutions (0, 1, 5, and 10 ppm) from the mixed metal 100 ppm solution using volumetric pipets and flasks. Aliquots of preserved drainage sample and the prepared standard solutions were placed on the autosampler for atomic absorption analysis at wavelengths of 248 and 279.5 nm to quantitate Fe and Mn, respectively. Students removed the heated precipitation samples from the hot plate to allow the solids to settle overnight.

The following day, the precipitated sulfate solids were filtered onto a tared Whatman filter paper using a Buchner funnel vacuum apparatus. The recovered solids and filter paper were then placed in a 100 °C oven for 15 min to remove any residual water, equilibrated to room temperature, and then weighed on the analytical balance. If the solids from the blank sample weighed more than 5 mg, the weight of the blank solids was subtracted from the weight of the neat sample solids. The actual concentration of sulfate ion in ppm (mg/L) in the neat drainage sample was then determined using the following equation:

$$\text{sulfate (ppm)} = \text{mg barium sulfate} \times \frac{0.412\ \text{mg sulfate ion}}{1.0\ \text{mg barium sulfate}} \times \frac{1}{100\ \text{mL}} \times \frac{1000\ \text{mL}}{1\ \text{L}}$$

Students received the results for each metal of interest (Fe, Mn, Al) from the atomic absorption analysis for their sample along with quality control parameters (absorbance value for the blank and the standard curve correlation coefficient) from the autosampler run. Students were required to evaluate the quality control parameters for acceptance of values before adding their results to the collective data spreadsheet.

HAZARDS

All chemical solutions are typical laboratory reagents; however, ingestion of large amounts of barium compounds can lead to gastrointestinal and cardiac health effects. The concentrated hydrochloric and nitric acids are corrosive and should be handled carefully and with gloves when being added to sample solutions.

■ STUDENT RESULTS

An example of the results on the collective data spreadsheet is presented in Table 2. Note that the aluminum results were supplied by the instructor since a nitrous oxide–acetylene oxidant/fuel combination for the atomic absorption instrument was unavailable. Students measured sample pH values to within ±5% of the true value and recovered sulfate ion with an average of 93%. Metals were detected within an average range of 88–150% of expected concentration, with the upper end of the range due to variation in results for samples with concentrations ≤ 1 ppm. All blank samples were acceptable (absorbance < 0.005), and correlation coefficients for each metal absorbance standard curve exceeded 0.90.

Table 2. Collective Data from Student AMD Sample Analyses

Sample Source	pH	SO_4^{2-} (ppm)	Fe (ppm)	Mn (ppm)	Al[a] (ppm)
Mine drainage source	4.69	579.7	14.903	11.6623	6.76
Drainage after settling pond	4.07	449.9	1.8154	11.6020	6.77
Drainage after VFP	7.37	486.2	1.8114	11.5708	0.02
Drainage after MRU	6.81	414.5	0.6507	10.4730	0.03
Drainage after oxic limestone bed	7.14	412.0	0.3431	0.6180	0.03

[a] Al results provided by instructor.

For the postlaboratory exercise, students reported their sample data (Table 3) using SOP specific templates and then evaluated the chemistry and effectiveness of the remediation steps using the collective data spreadsheet (Table 3). Most students correctly explained that samples exhibiting increased pH values after vertical flow pond (VFP) and the final oxic limestone bed steps were due to the presence of limestone (alkaline material) in these treatments that neutralized acid in the mine drainage flow. In addition, reports readily identified the remediation steps that are the most effective for removing two of the three metals. Students could rationalize the necessity of locating the settling pond early in the tract based on previous information that iron levels must be abated to improve oxidation of manganese as pH levels approach more neutral conditions. Students calculated the overall efficiency for removal of each metal (all above 95%) and the sulfate (30%) over the entire remediation series, and most correctly concluded that the groundwater is most likely being impacted by mine drainage flow somewhere around the VFP or MRU (metal removal unit) stages.

Table 3. Assessment of Student Performance ($n = 6$)

Laboratory Data Obtained from Simulated Mine Drainage Samples	Percent Student Completion
(1) Calibration curve with R^2 value >0.90 from dilution of 100 ppm standard metal solution	100%
(2) Sample sulfate concentration determination within 20% of prepared sample value	80%
(3) Determination of sample pH within 5% of prepared sample value	100%
Interpretation of Experimental Data from Simulated Mine Drainage Samples	**Percent Student Completion**
(1) Proper identification and explanation of the chemical remediation processes using alkaline materials that resulted in increased pH values	80%
(2) Adequate explanation of chemistry in the remediation step exhibiting the largest decrease in iron concentration before the precipitation of Mn	80%
(3) Correct calculation of percent decrease in metals and sulfate ion concentrations throughout the entire remediation tract	90%
(4) Identification of the most likely location for leakage into ground well water from the remediation tract based on well water testing results and class data	80%

■ DISCUSSION AND CONCLUSIONS

The experimental case study presented here expands the vision of forensic chemistry outside of the typical criminalistics field and increases student exposure to additional chemical techniques not typically conducted in undergraduate forensic chemistry courses. Student data obtained from these new techniques were reliable for interpreting how the different steps in the remediation tract were removing the harmful metals present and neutralizing the acidity in the mine drainage. In addition, the unique trends in each metal's removal throughout the series of treatment steps allowed students to pinpoint the potential locations where the drainage flow may be impacting the groundwater that supplies the residential well. The robust techniques for analysis of pH, sulfate, and metals described here permit applicability of this case study experiment to other courses: the same techniques (pH, sulfate precipitation, and atomic absorption) were incorporated into a laboratory exercise focused on comparing AMD treatment strategies that was developed for a separate environmental chemistry course populated by six integrative science students. The data collected in this course exhibited success similar to that obtained for the forensic chemistry course study presented here.

Expansion and flexibility of various aspects of the AMD case study can be useful in addressing additional pedagogical needs and goals. In the absence of a flame atomic absorption spectrometer, the concentrations of iron and manganese can be determined using UV–vis spectrophotometric methods involving complexation with 1,10-phenanthroline[22,23] and reaction with potassium iodate,[24,25] respectively. Demonstration of additional quality control parameters could be incorporated by including a duplicate aliquot from the drainage samples for the gravimetric sulfate determination and secondary check solutions for the calibration curves generated by the pH meter and atomic absorption spectrometer. Additional laboratory exercises previously published in this *Journal*[26,27] can be added to explore iron solubility and the use of sulfate reducing bacteria in mine drainage remediation. A comparative study could also be conducted by investigating the effectiveness of treatment steps from an alkaline mine drainage remediation tract.

Overall, students were receptive to the challenge of gravimetric analysis versus qualitative forensic chemical testing and of the use of flame atomic absorption spectroscopy as a welcome break from the more common forensic instruments (FTIR and GC). They applied their technical and problem-solving skills successfully to produce and interpret data in a traceable and accurate manner that is necessary for any forensic field. Students verbally noted that they enjoyed a new perspective: outcomes of the AMD case study produced forensic data to investigate and solve a current environmental problem as

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opposed to those of previous forensic experimental scenarios focusing on the confirmation of criminal activity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.9b00765.

Instructor preparation notes (PDF, DOCX)
Standard operating procedures for abandoned mine drainage (PDF, DOCX)
AMD lab scenario (PDF, DOCX)
Raw AA data for AMD samples (PDF, DOCX)

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Notes

The author declares no competing financial interest.

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■ REFERENCES

(1) Nabais, J. M. V.; Costa, S. D. A Forensic Experiment: The Case of the Crime at the Cinema. *J. Chem. Educ.* **2017**, *94* (8), 1111–1117.

(2) Cresswell, S. L.; Loughlin, W. A. An Interdisciplinary Guided Inquiry Laboratory for First Year Undergraduate Forensic Science Students. *J. Chem. Educ.* **2015**, *92* (10), 1730–1735.

(3) Smith, M. J.; Vale, I. C.; Gray, F. M. Identification of Paper by Stationary Phase Performance. *J. Chem. Educ.* **2014**, *91* (10), 1679–1683.

(4) Schurter, E. J.; Zook-Gerdau, L. A.; Szalay, P. Analysis of a Suspected Drug Sample. *J. Chem. Educ.* **2011**, *88* (10), 1416–1418.

(5) Szalay, P. S.; Zook-Gerdau, L. A.; Schurter, E. J. A Multi-Technique Forensic Experiment for a Nonscience-Major Chemistry Course. *J. Chem. Educ.* **2011**, *88* (10), 1419–1421.

(6) Specht, K. M.; Boucher, M. A. A Forensic-Themed Case Study for the Organic Lab. *J. Chem. Educ.* **2009**, *86* (7), 847–848.

(7) Bender, S.; Lillard, S. J. Was the Suspect in Contact with the Victim? An Instrumental Methods Experiment for the Analysis of Single Fibers Using FT-IR Microscopy. *J. Chem. Educ.* **2003**, *80* (4), 437–440.

(8) Thompson, R. B.; Thompson, B. F. Forensic Analysis of Paper. *Forensic Teacher.* **2016**, *10* (29), 18–23.

(9) Komal, S.; Kauer, H. H.; Rajshree, R. Differentiation Inkjet Printer Inks by Thin Layer Chromatography and High Performance Liquid Chromatography. *Res. J. Forensic Sci.* **2015**, *3* (7), 1–7.

(10) Joshi, B.; Verma, K.; Singh, J. A Comparison of Red Pigments in Different Lipsticks Using This Layer Chromatography. *J. Anal. Bioanal. Tech.* **2013**, *4* (1), 157–160.

(11) Causin, V.; Casamassima, R.; Marega, C.; Maida, P.; Schiavone, S.; Marigo, A.; Villari, A. The Discrimination Potential of Ultraviolet - Visible Spectrophotometry, Thin Layer Chromatography and Fourier Transform Infrared Spectroscopy for the Forensic Analysis of Black and Blue Ballpoint Inks. *J. Forensic Sci.* **2008**, *53* (6), 1468–1473.

(12) Anscombe, N. Beyond CSI: Environmental Forensics Picks Up in Europe. *Science/AAAS Website, Careers*; posted August 3, 2007. DOI: 10.1126/science.caredit.a0700110.

(13) United States Environmental Protection Agency. Criminal Enforcement. https://www.epa.gov/enforcement/criminal-enforcement (accessed Dec 2019).

(14) USGS Pennsylvania Water Science Center. Energy Studies. Coal-Mine-Drainage Projects in Pennsylvania. October 2010. http://pa.water.usgs.gov/projects/energy/amd/index.php (accessed Dec 2019).

(15) PA Department of Community and Economic Development, Grant Program. Abandoned Mine Drainage Abatement and Treatment Program (AMDATP). https://dced.pa.gov/programs/abandoned-mine-drainage-abatement-treatment-program-amdatp/ (accessed Dec 2019).

(16) Johnson, D. B.; Hallberg, K. B. Acid Mine Drainage remediation options: a review. *Sci. Total Environ.* **2005**, *338*, 3–14.

(17) Hedin, R.; Weaver, T.; Wolfe, N.; Watzlaf, G. Effective Passive Treatment of Coal Mine Drainage. *Technical paper presented at the 35th Annual National Association of Abandoned Mine Land Programs Conference, September 23, 2013, Daniels, West Virginia.* http://www.hedinenv.com/pdf/NAMLP_Effective_Passive_Treatment_Paper.pdf (accessed Dec 2019).

(18) *Treating Acid Mine Drainage from Abandoned Mines in Remote Areas*; US Department of Agriculture, Forest Service, Technology and Development Program: Missoula, MT, October 1998.

(19) *How the AAS Works*; Victorian Space Science Education Center: Australia. https://www.youtube.com/watch?v=L3OFSJ8ZHog (accessed Dec 2019).

(20) *Atomic Absorption Spectrometry*; Maryville University: Pennsylvania. https://www.youtube.com/watch?v=SDbC4a2n4W8 (accessed Dec 2019).

(21) *Flame Atomic Absorption Spectroscopy Demonstration*; St. Mary's University of San Antonio: Texas. https://www.youtube.com/watch?v=_KZjb9G3hB8 (accessed Dec 2019).

(22) *CHEM 334 Quantitative Analysis Laboratory Spectrophotometric Determination of Iron*; Colorado State University, 2018.10.29. https://sites.chem.colostate.edu/diverdi/C334/experiments/04_spectrophotometric_determination_of_iron.pdf (accessed Dec 2019).

(23) *Molecular Absorption Spectroscopy: Determination of Iron with 1,10-Phenanthroline. Department of Chemistry*; University of Kentucky. https://m.tau.ac.il/~chemlaba/Files/Fe%20Phenanthroline1.pdf (accessed Dec 2019).

(24) *Determination of Manganese in Steel*; Department of Chemistry, Bogazici University. http://www.chem.boun.edu.tr/wp-content/uploads/2014/04/Lab-Procedure.pdf (accessed Dec 2019).

(25) *Measuring Manganese Concentration Using Spectroscopy*; Department of Physical Sciences, Santa Monica College. https://www.smc.edu/AcademicPrograms/PhysicalSciences/Chemistry/Lab-Manual/Documents/Chemistry_11_Experiments/Mn_Lab.pdf (accessed Dec 2019).

(26) Meighan, M.; MacNeil, J.; Falconer, R. Determining the Solubility Product of $Fe(OH)_3$: An Equilibrium Study with environmental Significance. *J. Chem. Educ.* **2008**, *85* (2), 254–255.

(27) Hauri, J. F.; Schaider, L. A. Remediation of Acid Mine Drainage with Sulfate Reducing Bacteria. *J. Chem. Educ.* **2009**, *86* (2), 216–218.